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REGULAR ARTICLE

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A DFT study on the hydrated V_2O_5-TiO_2-anatase catalyst: stability of monomeric species

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Abstract A combined cluster and periodic study has been carried out to elucidate the stability of hydrated species on the vanadia/titania catalyst. First, the hydration of a V_2O_5 cluster was analyzed for the successive adsorption of one to four water molecules. The dimeric skeleton is found to be preserved at a low water concentration. However, after the adsorption of four water molecules on the dimer, it is found to break to generate stable monomeric $OV(OH)_3$ units. The two moieties are related by the equation:
$V_2O_5 + 3H_2O \rightarrow 2OV(OH)_3$
Such $OV(OH)_3$ units have been taken as a monomer model for the periodic representation of the vanadia/titania catalyst. On the (100) surface, the $OV(OH)_3$ moieties are anchored by three V–O–Ti bonds to the support surface in a pyramidal arrangement. The vanadyl V=O bond is found to be very stable.

Keywords Density functional calculations · Catalysis · Chemisorption · titanium oxide · Vanadium oxide

1 Introduction

The vanadia/titania catalyst is widely used in industrial plants for the removal of nitrogen oxides (SCR reaction) [1]:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

The efficiency of this catalyst has been attributed to the dispersion of the active phase, V_2O_5, on the support, TiO_2-anatase. Such dispersion results in the presence of dimeric and monomeric species depending on the concentration [2–8]. Since the reaction takes place in a wet environment, and since water is a final product of the reaction, it is crucial to understand the interaction of H_2O with the catalyst. The aim of this paper is to analyze the hydration of V_2O_5 and the stability of monomeric species. Both species are related by the following equation:

$$V_2O_5 + 3H_2O \rightarrow 2OV(OH)_3$$

Little is known about the hydrated structures involving vanadium with the oxidation number +5. The stability of the different species in solution critically depends on concentration and pH. Speciation of vanadium V^{+5} in water solution involves complex equilibrium between various mono- and oligonuclear clusters. In dilute solutions at pH 7, the dominant species is $[H_2VO_4]^-$ [9]. Lowering the pH results in a double protonation of such species and the predominant product is usually formulated as VO_2^+, which is believed to be six-coordinated with a cis-VO_2^+ moiety and four complexed H_2O molecules [9]. In basic conditions, mono- and di- vanadates stabilize in their tetrahedral VO_4^{3-} and $V_2O_7^{4-}$ forms. The tetrahedral environment is very favorable for the vanadium atom in many compounds like $OVCl_3$, NH_4VO_3 or Na_3VO_4.

The SCR reaction and the vanadia/titania catalyst have generated a great interest from the theoretical point of view due to the poor knowledge on the processes taking place at an atomic level. In particular, the structure of the catalyst and the role of the different sites are still a matter of controversy. Few groups have developed a special interest for the theoretical description of the vanadia/titania catalyst. Jug and coworkers have investigated by semiempirical calculations on cluster models the adsorption of small molecules on (001)-V_2O_5 [10], (100)-anatase [11] and a vanadia/titania model [12]. They also propose a complete reaction mechanism for the SCR reaction based on a V_2O_5–TiO_2 cluster [13]. Vittadini and Selloni [14] have recently studied by periodic DFT calculations the structure and reactivity of a V_2O_5–TiO_2(001) model and conclude the stability of monomeric species at low vanadium coverage, which convert to divanadate units at higher coverage. Zhanpeisov [15] has studied the effect of the support on the reactivity of the catalyst by cluster Hartree–Fock calculations. Some other studies focused on

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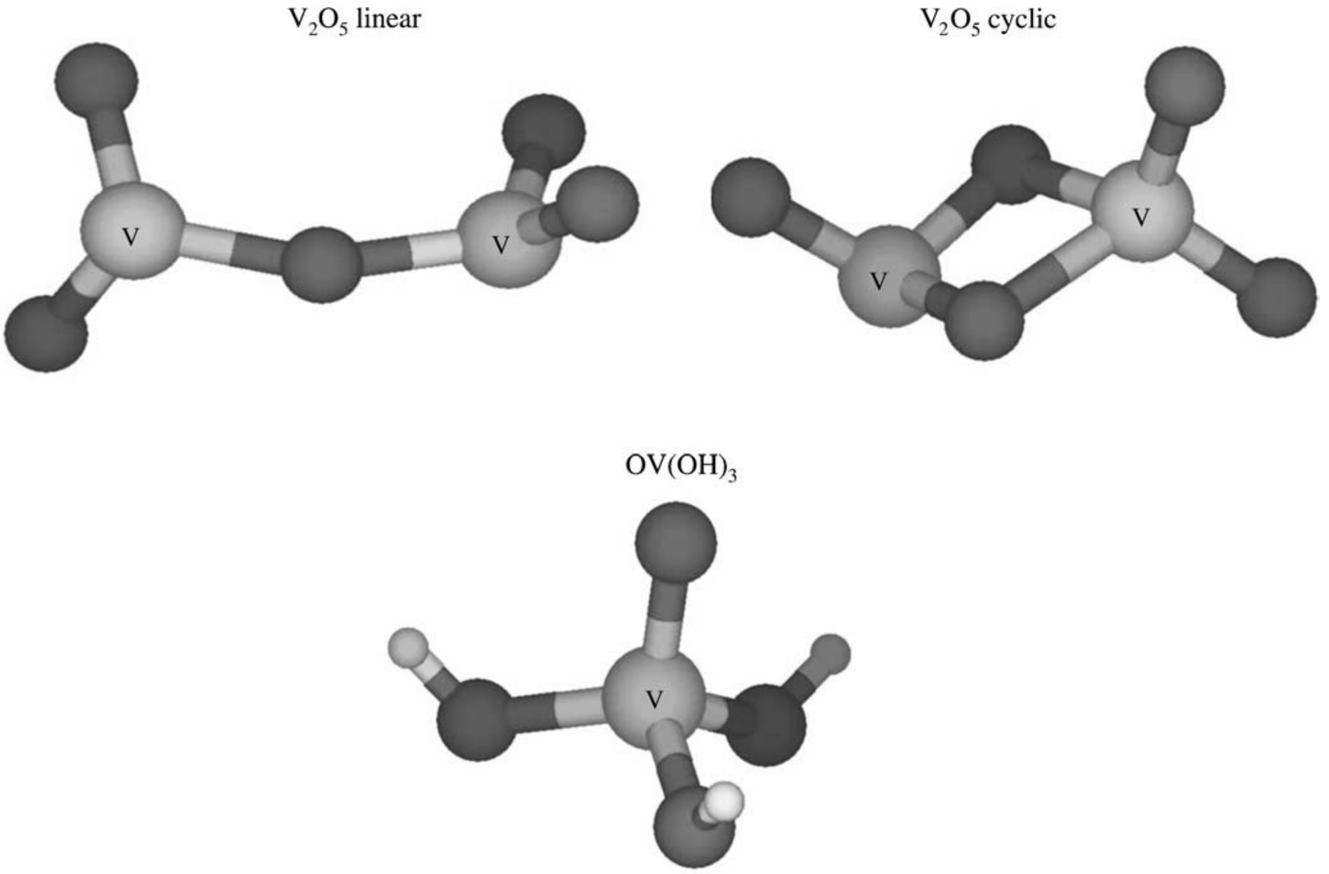

Fig. 1 Gas phase V_2O_5 clusters: *left*: linear O_2VOVO_2; *right*: cyclic OVO_2VO_2; *bottom*: monomeric $OV(OH)_3$

the adsorption of small molecules on pure $V_2O_5(001)$ [16–18] or the effect of the support [7]. Our group has devoted a research line to the modeling of the SCR reaction on the V_2O_5/TiO_2 catalyst [19–22]. We focus on the effect of the support in the dispersion of the catalyst and the role of the interface V–O–Ti sites [19]. We hope to provide important information on the stability of dimeric and monomeric species of V_2O_5 dispersed on anatase-TiO_2, and their reactivity towards hydration.

2 Methods and models

Our strategy consists of modeling the V_2O_5 active phase by a cluster and analyzing the successive adsorption of one to four water molecules. Hydration leads to the break of the dimeric structure to stabilize monomeric $OV(OH)_3$ species. We will then construct a periodic model by making the $OV(OH)_3$ unit interact with an anatase slab. The aim is to obtain a periodic model for the monomeric species observed experimentally.

The cluster calculations were carried out at a B3LYP level with a DB-31G* basis set for all atoms. The Gaussian98 [23] code was used. We have not corrected for BSSE, so the binding energies are overestimated. Two main structures have been considered for the V_2O_5 units: a linear O_2VOVO_2 and a cyclic OVO_2VO_2 as in Fig. 1. The latter is the most favorable by 0.68 eV (0.82 eV [24], 0.62 eV[25]). The reason for the higher stability is the presence of a tetrahedral vanadium atom, which is a favorable environment for this atom, while for the linear isomer the two vanadium centers are three-fold coordinated. Hydration by three water molecules leads to pyramidal $OV(OH)_3$ units, displayed in Fig. 1. The reaction

$$V_2O_5 + 3H_2O \rightarrow 2OV(OH)_3$$

is exothermic by 3.92 eV according to our B3LYP calculations [19]. In the $OV(OH)_3$ unit, the vanadium atom presents an oxidation state of +5 as for V_2O_5.

For the periodic model, all the total energy calculations have been performed using the VASP program [26, 27]. In this code, the Kohn–Sham equations are solved within the GGA PW91 functional [28, 29]. The core electrons are described by ultrasoft pseudopotentials [30, 31] and the valence electrons by plane-wave basis set with a cut-off energy of 400 eV. For the Brillouin-zone integration, a $5 \times 5 \times 1$ Monkhorst-Pack special k-points grid was used.

We take as model the (100) anatase surface represented in Fig. 2. This surface is found in commercial powders [32] and presents a convenient geometry for the interaction of the $OV(OH)_3$ unit on it. The model consists of a 2×1 (100) unit cell containing two TiO_2 layers, with only the first one optimized. This is a simple system but contains the main

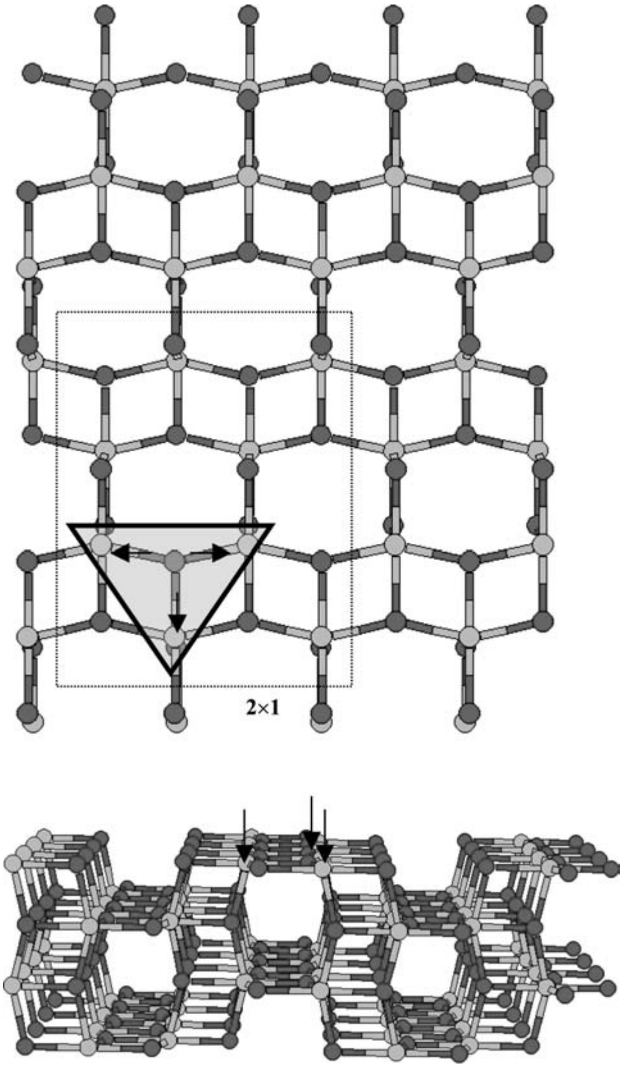

Fig. 2 Anatase (100) surface, the unit cell is shown in shaded lines. A triangle of three Ti atoms where $OV(OH)_3$ pyramids can anchor is indicated

features required for the model: a sufficient area to ensure the absence of interaction between two monomer units, and a local arrangement containing a triangle of three Ti atoms as shown in Fig. 2 to anchor the $OV(OH)_3$ pyramid. We then situate the OVO_3 skeleton in the vicinity of the triangular Ti arrangement and distribute the three H on the surface sites. As a result, three O–Ti bonds are formed between the monomer OVO_3 and the support. Other configurations involving only two bonds between the monomer and the support are found to be less favorable by 2 eV. A systematic study of the different distribution of H on the surface is carried out.

3 Results

3.1 Water adsorption on clusters

We evaluate in this section the adsorption mode of water on the clusters and the successive adsorption of one to four molecules. Linear and cyclic V_2O_5 units as shown in Fig. 1 are used as substrates. Adsorption always takes place on the uncoordinated vanadium center so as to reach a tetrahedral environment on this atom. Adsorption energies are calculated as

$$E_{\mathrm{ads}} = (nE_{\mathrm{H_2O}} + E_{\mathrm{V_2O_5}} - E_{n\mathrm{H_2O+V_2O_5}})$$

where n is the number of water molecules, and E_{ads} is positive for exothermic processes. Table 1 shows the adsorption energy values for the different adsorption systems.

Table 1 Adsorption energy values for the V_2O_5 clusters upon water adsorption, in eV. Positive values indicate exothermic processes

n H_2O			E_{ads}
0	O_2VOVO_2	Linear V_2O_5	0.68*
	OVO_2VO_2	Cyclic V_2O_5	0.00*
1	$(H_2O)O_2VOVO_2$	Molecular on linear V_2O_5	1.50
	$(H_2O)OVO_2VO_2$	Molecular on cyclic V_2O_5	1.96
	$(OH)O_2VOVO(OH)$	Dissociative on linear V_2O_5	1.68
	(OH)OVO2VO(OH)	Dissociative on cyclic V_2O_5	2.98
2	$(HO)_2OVOVO(OH)_2$	Break of the VO_2V cycle	4.09
3	$(HO)_2OVOVO(OH)_2...H_2O$		4.75
	$2OV(OH)_3$		4.47
4	$2OV(OH)_3 + H_2O$		5.64

*Relative energy for the V_2O_5 clusters

Molecular adsorption of one H_2O is less favorable than dissociative for the two cluster models as shown in Table 1. Adsorption on the cyclic cluster is always more favorable, since it allows the two vanadium atoms to be tetrahedral. The most stable structure for the adsorption of one water molecule corresponds to its dissociation on the cyclic cluster to generate $(HO)OVO_2VO(OH)$ (Fig. 3A), with $E_{\mathrm{ads}} = 2.98$ eV. The adsorption of a second water molecule on this system also results in a dissociation of the adsorbate and a break of the cycle to preserve the tetrahedral coordination on each vanadium atom ($(HO)_2OVOVO(OH)_2$ see Fig. 3B). If a third water molecule is added to this system, it binds by hydrogen bonds as shown in Fig. 3C. The reason for that is that all vanadium atoms already possess the tetrahedral environment; further dissociation would lead to unfavorable five-fold coordinated metallic atoms. Another structure is possible for three water molecules on V_2O_5: it consists of two $OV(OH)_3$ units in interaction (Fig. 3E). At this point, this structure is 0.28 eV less favorable than 3C. Let us consider the adsorption of a fourth water molecule. On structure 3D, two water molecules bind to the VOV structure (Fig. 3F) while on the $2OV(OH)_3$ structure the two monomers stabilize and the fourth molecule binds by hydrogen bonds to these fragments (Fig. 3G). The latter now becomes more stable indicating that at high concentration of water the monomeric species stabilize, while at lower concentrations one would obtain the dimeric skeleton. However, the presence of a support could contribute to stabilize the monomeric species rather than the dimeric even at a low water concentration.

Finally, the formation of open-shell systems can be helpful for reactivity. The triplet states for the singlet systems described above are in the order of 0.85 eV higher in energy, which is not a high cost. For instance, the formation of an

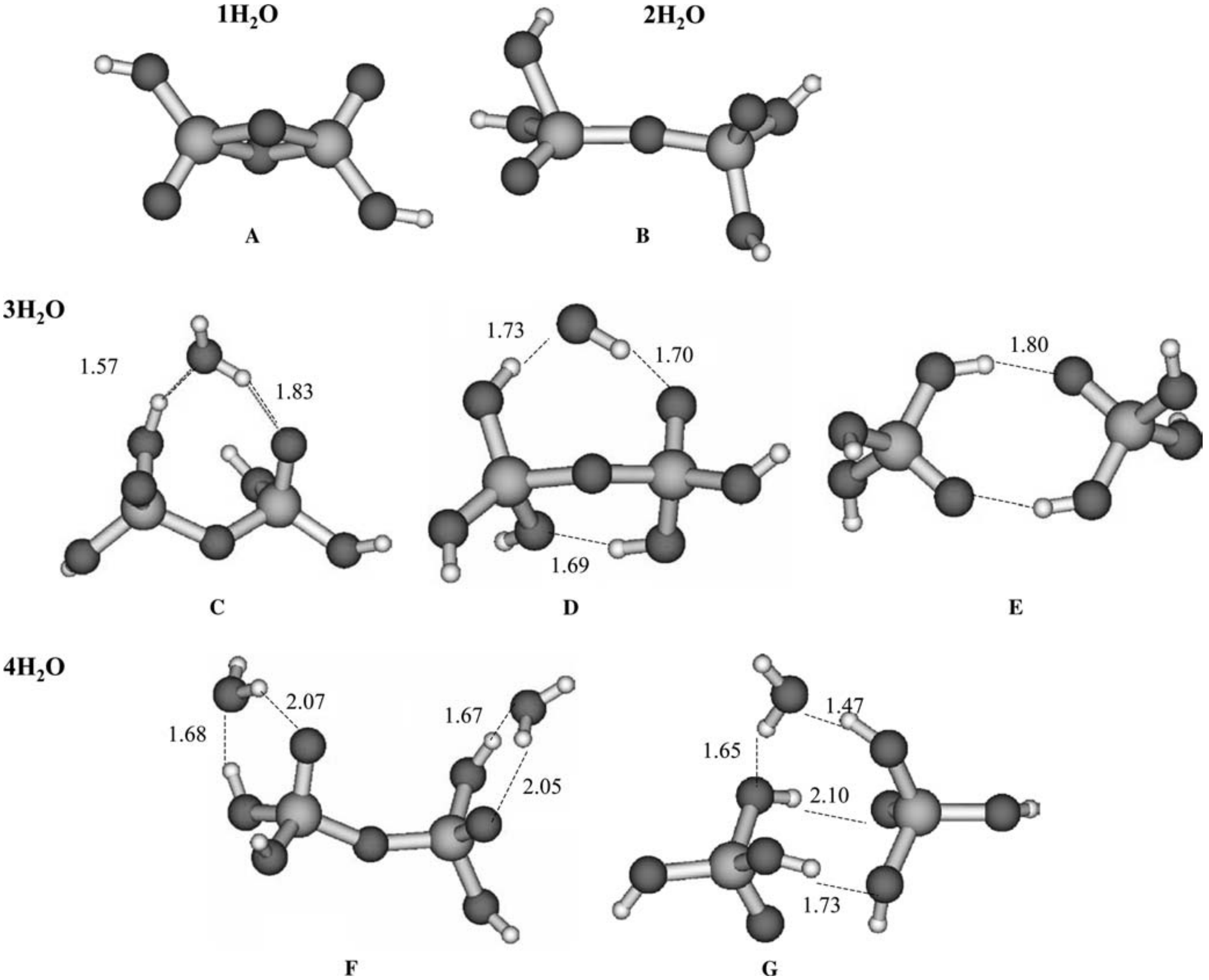

Fig. 3 Most stable structures for the hydration of V_2O_5. **A** one H_2O; **B** two H_2O; **C** three H_2O, most stable structure; **D** three H_2O, structure with decomposition into two monomeric species; **E** alternative three H_2O, structure with dissociation of the water leading to the OH radical (triplet state); **F** four H_2O, dimeric structure; **G** four H_2O, structure with decomposition into two monomeric species, the most stable structure

OH radical in weak interaction with a $(HO)_2OVOV(OH)_3$ complex where the vanadium atom is V(+4) (leading to structure 3D in a triplet state) is less stable than structure 3C by 0.80 eV. In some cases, like the molecular adsorption of water on V_2O_5, the difference is less than 0.43 eV. This could be helpful for reactivity.

In conclusion, cluster calculations show that the dimeric skeleton of V_2O_5 is preserved at low water concentrations. The monomeric species $OV(OH)_3$ are stabilized under hydration at high water concentrations or by interaction with the support as proposed in the literature [7].

3.2 Periodic calculations

The investigation of the hydration of V_2O_5 clusters leads to the stability of monomeric $OV(OH)_3$ at high water concentrations. In the limit of diluted vanadium in water, the monomeric species exist in the form $[O_2V(OH)_2]^-$ at pH 7 (see ref. [9] and references therein). The following step is to build a periodic model of the anatase support including the active phase, in this case the monomer $OV(OH)_3$. As we justify in Sect. 2, we have selected the (100) anatase surface. We first make the OVO_3 fragment interact with the surface as in Fig. 4 and then we distribute the H atoms on the slab oxygen sites. Note that the $OV(OH)_3$ monomers possess V^{+5} atoms; the H atoms are necessary to preserve this oxidation state (if there were no hydrogen, atoms the system would be oxidized) and cannot be omitted in the model. The monomer stability in a real system would be sensitive to the thermodynamic conditions, in particular to the H and O chemical potentials. We will now discuss the geometry of the basic model and the distribution of the H atoms on the different sites.

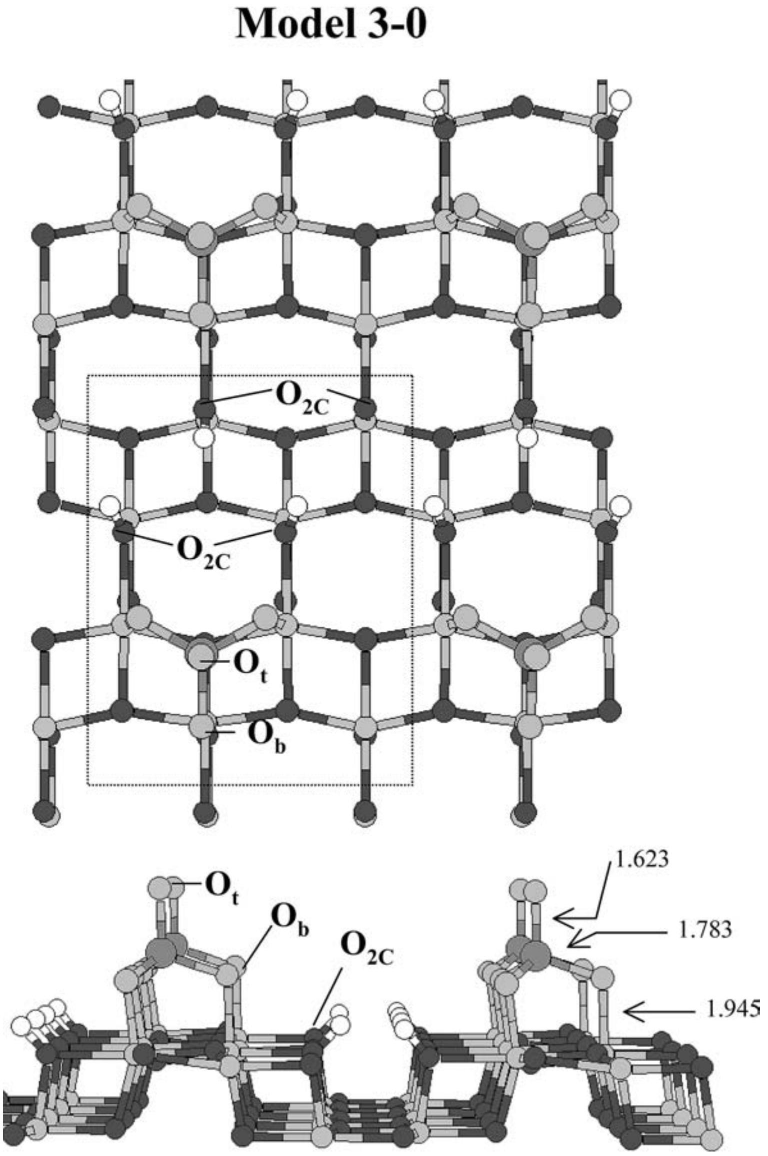

Fig. 4 OVO_3 fragment interact with the surface and the H with the surface oxygen atoms, O_{2c}. OVO_3 pyramids contain a terminal oxygen O_t and three bridging oxygen O_b atoms binding to surface titanium atoms

The OVO_3 pyramids contain a terminal oxygen O_t and three bridging oxygen O_b atoms binding to surface titanium atoms. The former constitutes a vanadyl V = O bond pointing out of the plane with a V = O distance 1.623 Å, while the latter are V–O–Ti bonds with distances of 1.785 and 1.945 Å. This arrangement is possible since the Ti atoms on the surface are disposed in a zig-zag manner and form triangles where the pyramid can anchor (see Figs. 2 and 4). In the surface, there are also four dicoordinated oxygen sites O_{2C}. The distribution of the three H atoms is done on both monomer and surface sites. The notation is as follows: first number indicates the H on the surface, then the number of hydrogen on the O_b of the OVO_3 unit (V–O–Ti sites); the number of H on the terminal oxygen is easily obtained by subtracting the others from three. For instance, the model containing all the three H atoms on the surface sites is 3–0; that containing one H on the surface, one on O_b and one on O_t is 1-1 and so on. Adsorption energy is calculated as $(E_{\mathrm{OV(OH)_3}} + E_{\mathrm{slab}} - E_{\mathrm{OV(OH)_3/slab}})$ and is shown in Table 2.

Table 2 Adsorption energy of $OV(OH)_3$ on a 2 × 1 (100) cell slab

Model	E_{ads}
3–0	−0.02
2–1	0.96
2–0	0.93
1–2	1.21
1–1	1.33
0–3	0.98
0–2	0.89

Notation is: number of H on the surface – number of hydrogen on the O_{2C} of the VO_4 unit. The number of H on the terminal oxygen is easily obtained by subtracting the others from three. E_{ads} calculated as in the text (positive values indicate exothermic processes)

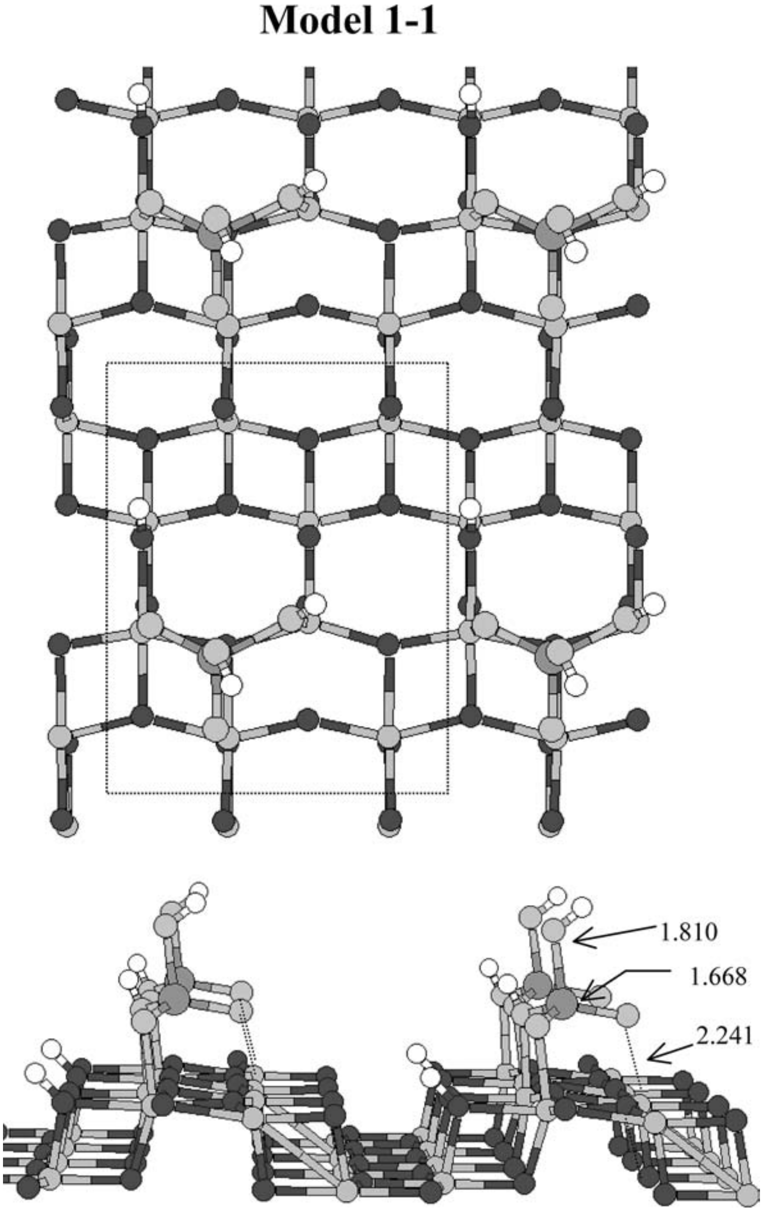

Fig. 5 Monomer adsorption: one H interacts with O_{2c} oxygen of the slab; the two others interact with OVO_3 fragment: one with O_t and the other with O_b. The Ti–O_b bond elongates and the V–O_b bond shortens regenerating a V=O bond

An analysis of the adsorption energy values shows that all the possible distributions of hydrogen on this skeleton including OVO_3 sites are close in energy, ranging from 0.89 to 1.33 eV. When the hydrogen is placed on the surface sites, leaving bare the OVO_3 unit (model 3–0), the adsorption energy is slightly endothermic, −0.02 eV. This model is displayed in Fig. 4 and shows a V=O distance of 1.623 Å and V–O–Ti distances of 1.783 and 1.945 Å respectively. So, in the presence of a OVO_3 unit it is preferred not to have the hydrogen atoms exclusively on the surface. The presence of bare OVO_3 units anchored to the TiO_2 surface proposed in the literature is not supported by our calculations. The vanadate species VO_4^{3-} can only be found in water solution in basic conditions; at pH 7, the diprotonated $[O_2V(OH)_2]^-$ species is predominant. This is in line with previous experimental [33] and theoretical [19] results supporting that mixed catalysts would expose preferentially V–OH groups than Ti–OH.

Nevertheless, although the hydrogen atoms do not bind exclusively to the surface sites, they do not bind exclusively to the OVO_3 unit but rather distribute to occupy both the active phase and the substrate adsorption sites. The most stable conformation is that where each hydrogen atom is bonded to one surface, one O_b and one O_t (model 1-1 $E_{\text{ads}} = 1.33$ eV, Fig. 5). Let us examine closely these values.

Let us discuss the presence of one hydrogen atom on the OVO_3 unit and two on the surface sites. The H atom on the

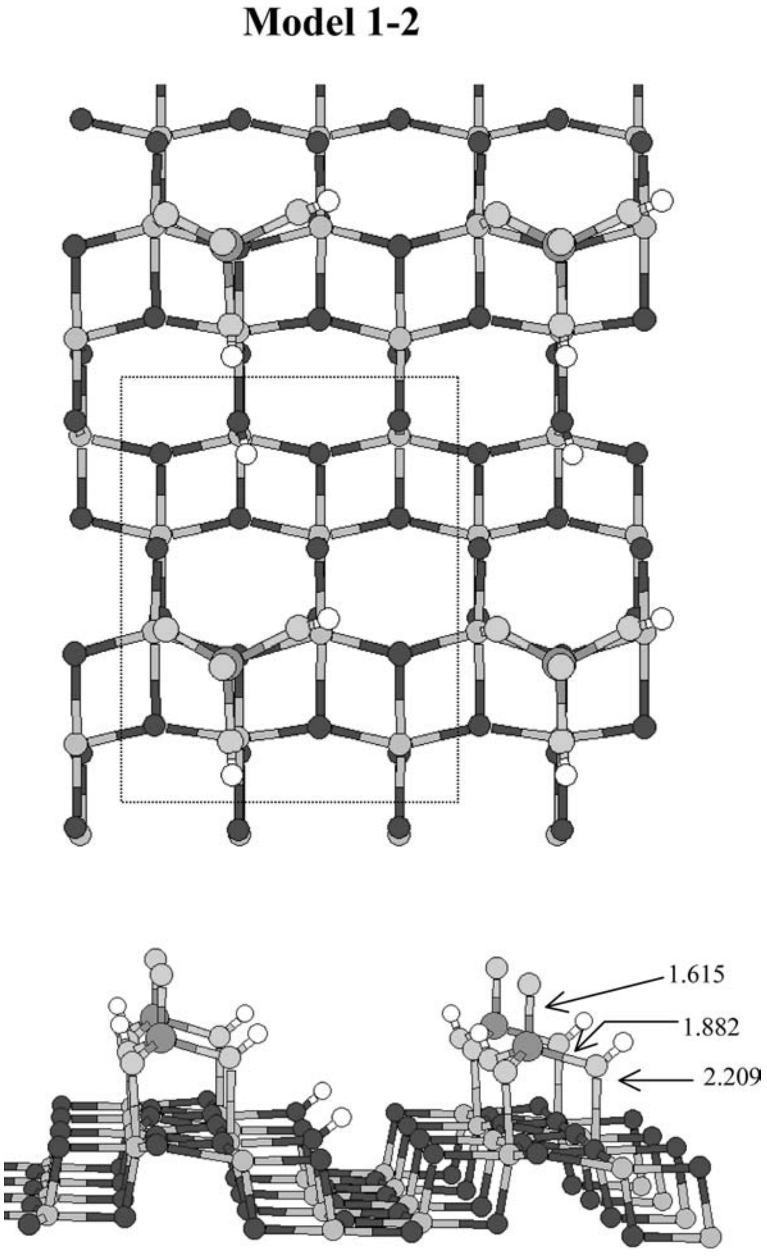

Fig. 6 Monomer adsorption: one hydrogen atom is on the surface oxygen atom, O_{2c}, and the two others on bridging O_b atoms of the monomer

monomer can be placed on a bridging or a terminal oxygen (models 2-1 and 2-0). They are very close in energy. The effect in the former geometry is to elongate the V–O–Ti bonds to values of 1.907 and 2.205 Å. The result is the formation of a hydroxyl group in weak interaction with the surface Ti sites. The 2-0 model presents almost identical V–O–Ti distances as for the 3-0 but the terminal V = O distance increases from 1.623 Å up to 1.803 Å. This is the typical value for a bridging atom and we find again a terminal hydroxyl group.

The presence of two hydrogen atoms on the OVO_3 unit leads to two isomers: the first with the two H on O_t and O_b, and the second with the two H on two O_b. The former, model 1-1, is the most stable of all the studied. As for the previous case, adsorption on the terminal oxygen results in an increase in the V = O bond length to 1.810 Å. An important feature is however observed for one of the non-protonated V–O–Ti groups: it decreases the V–O distance to 1.668 Å and becomes a terminal one in interaction with a surface Ti at 2.241 Å (see Fig. 5). In other words, it is formally a 1-2 model benefiting from a weak V = O•••Ti interaction. This isomer is more stable than the 1-2 model (Fig. 6, Table 2) by 0.12 eV. The two bridging bonds linked to H show higher distances to both V and Ti atoms, in the order of 1.88 and 2.22 Å and are indeed terminal hydroxyls in weak interaction with the surface; the third O_b stays closely bonded (1.696 and 2.127 Å).

We finally consider two models where the three hydrogen atoms are bonded only to the OVO_3 sites: models 0-3 and 0-2. The adsorption energy is rather smaller, $E_{ads} = 0.98$ and 0.89 eV respectively. The former shows the $OV(OH)_3$ unit floating on the surface at more than 2.30 Å, with V–O_b bonds around 1.83 Å and V = O 1.616 Å. For comparison, the gas-phase unit presents bonds of 1.783 and 1.542 Å respectively. The second isomer 0-2 also presents the formation of a short V=O bond upon reaction of the initially terminal oxygen with H, in weak interaction with a surface Ti.

In summary, the most stable systems from Table 2 leave one H atom on the surface and two on the OVO_3 unit. A possible explanation comes from considering $OV(OH)_3$ as an acid analogous to $OP(OH)_3$. Then, we have three acidic protons that can dissociate:

$$OV(OH)_3 \rightarrow O_2V(OH)_2^- + H^+$$

$$O_2V(OH)_2^- \rightarrow O_3V(OH)^{2-} + H^+$$

$$O_3V(OH)^{2-} \rightarrow VO_4^{3-} + H^+$$

It is well known that if the first ionization is the most exothermic, then the $O_2V(OH)_2^-$ species would be the most stable. If this species adsorbs on a slab and the H^+ on a surface O_{2C} site, we obtain the 1-1 and 1-2 models which are those showing higher E_{ads} values. Further dissociation would lead to highly charged species and distribution of two or three H^+ atoms on the surface sites. This would explain the higher stability found for the 1-1 and 1-2 models. Note that in any case these acidic decompositions leading to charged species do not involve any electron transfer: the vanadium atom possesses an oxidation state of +5 in all the intermediates. The $[O_2V(OH)_2]^-$species are predominant in a water solution at pH 7 [9].

Finally, let us mention that our study aimed at determining stable monomeric structures on the anatase support. One has to take into account the dynamics of a real system as far as the hydrogen distribution is concerned. Thus, the real surface distribution should rather be a dynamic system in which hydrogen atoms move on the reactive sites.

4 Conclusions

Cluster and periodic calculations were carried out to investigate the hydration of V_2O_5 species and the stability of monomer species.

1. Monomers become more stable than dimers at high water concentrations. They are represented in our models as $OV(OH)_3$ species.
2. Such species strongly bind to the support (100) anatase forming pyramidal units. They show a vanadyl V=O bond pointing outwards and three V–O–Ti bonds.
3. Hydrogen atoms in the $OV(OH)_3$ unit are necessary in the model to maintain a V^{5+} state. They distribute between the monomer and the support sites. In real systems, the system is not expected to have a determined configuration of H atoms in the system but rather a dynamic process.
4. The most stable systems present one hydrogen on the support sites and two on the monomer (models 1-1 and 1-2), with an adsorption energy of 1.21 and 1.33 eV respectively. These systems evolve to the formation of a stable V=O bond weakly interacting with a surface Ti. This is an indication of the high stability of the V=O bond. However, the evolution from 1-1 to 1-2 indicates possible fluctuation in the coordination of the various O atoms. The V–O–Ti sites would be more reactive.
5. The model where the OVO_3 unit is bare and the H atoms are exclusively on the surface sites (model 3-0) is not stable according to our calculations.
6. The $OV(OH)_3$ species can be thought of as an acid analogous to $OP(OH)_3$. The first ionization is the most favorable and leads to $O_2V(OH)_2^-$ anchored as a pyramid to Ti sites, and a H^+ that would adsorb on the support oxygen sites. This would explain the stability of the systems with only one H on the support.

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